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(54) Title: HIGH LATHERING AND HIGH DEPOSITING SHAMPOOS WITH MILD SURFACTANT SYSTEM (57) Abstract <p>Provided is a mild, high lathering shampoo composition with high deposition of functional materials, the shampoo composition comprising: (a) from about 5 % to about 40 %, by weight, surfactant system comprising: (i) from 80 % to about 99 %, by weight of the surfactant system, anionic surfactants which are alkyl ethoxylated sulfates and alkyl sulfates in a ratio between about 1:1 and 1:0; and (ii) from about 1 % to 20 %, by weight of the surfactant system, polyhydroxy fatty acid amide surfactants; (b) from about 0.05 % to about 25 %, by weight, functional materials; and (c) from about 35 % to about 95 %, by weight, water.</p>		

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HIGH LATHERING AND HIGH DEPOSITING SHAMPOOS WITH MILD SURFACTANT SYSTEM

Technical Field

The present invention relates to shampoo compositions containing functional materials such as conditioning agents, styling agents or antidandruff agents. In particular, the present invention relates to mild shampoo compositions that are high lathering and provide high deposition of functional materials.

Background of the Invention

Acceptable shampoo compositions should cleanse the hair and scalp and be safe to the user. However, preferred shampoos will provide more benefits than simple cleanliness and safety. For example, it is desirable to use a mild surfactant system in shampoos so that the shampoos are non-irritating and gentle to the scalp.

It is also desirable to incorporate various functional materials in shampoos to provide benefits in addition to cleansing. Examples of such functional materials include conditioning agents, styling agents, antidandruff agents, and the like. Preferred shampoos will provide high deposition of the functional materials on the hair and scalp, so that the materials can provide their intended benefits. For instance, conditioning agents should be efficiently deposited on the hair during use of the shampoo, so that the agents are not rinsed away and can provide good conditioning benefits. Similarly, antidandruff agents should be efficiently deposited on the scalp to provide good antidandruff performance.

Another important parameter in the formulation of shampoos is lathering. The consuming public often associates high lathering with effective cleaning, and typically prefers high lathering shampoos to low lathering shampoos from an aesthetic standpoint.

Typical mild shampoo formulations utilize high levels of nonionic, cationic and amphoteric surfactants in the presence of anionic surfactants to obtain good mildness characteristics. However, the lather volumes of these formulations tend to be appreciably lower than regular anionic surfactant-based shampoo formulations.

The advantage of the present invention is the discovery that shampoos containing a particular surfactant system not only provide desirable mildness, but also provide the benefits of high lathering and

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high deposition of functional materials. The surfactant system is a combination of certain anionic surfactants and polyhydroxy fatty acid amide surfactants in particular amounts and ratios. This invention is described in further detail hereinbelow.

Unless otherwise indicated, all percentages and ratios are calculated on a weight basis. Unless otherwise indicated, ingredients are based on the active level and, therefore do not include carriers or by-products that may be included in commercially available materials.

Summary of the Invention

The present invention provides a mild, high lathering shampoo composition with high deposition of functional materials, the shampoo composition comprising:

- (a) from about 5% to about 40%, by weight, surfactant system comprising: (i) from 80% to about 99%, by weight of the surfactant system, anionic surfactants which are alkyl ethoxylated sulfates and alkyl sulfates in a ratio between about 1:1 and 1:0; and (ii) from about 1% to 20%, by weight of the surfactant system, polyhydroxy fatty acid amide surfactants;
- (b) from about 0.05% to about 25%, by weight, functional materials; and
- (c) from about 35% to about 95%, by weight, water.

The shampoo compositions of this invention advantageously provide the desirable combination of mildness, high lathering, and high deposition of functional materials such as conditioning agents, styling agents or antidandruff agents.

Detailed Description of the Invention

Surfactant System

The shampoo compositions of the present invention contain a particular surfactant system that has been found to exhibit a desirable combination of benefits: mildness to the scalp, high lathering, and high deposition of functional materials such as conditioning agents, styling agents, antidandruff agents and the like. The shampoos contain from about 5% to about 40% by weight surfactant system, preferably from about 7% to about 35% by weight, and more preferably from about 12% to about 20% by weight. The surfactant system comprises: (i) from 80% to about 99%, by weight of the surfactant system, anionic surfactants which

ar alkyl thoxylated sulfates and alkyl sulfates in a ratio between about 1:1 and 1:0; and (ii) from about 1% to 20%, by weight of the surfactant system, polyhydroxy fatty acid amide surfactants.

Alkyl Ethoxylated Sulfate and Alkyl Sulfate Surfactants

As mentioned above, the surfactant system of the present shampoo compositions comprises from 80% to about 99% by weight of the surfactant system, preferably from about 85% to about 95% by weight, anionic surfactants which are alkyl ethoxylated sulfates ("AES") and alkyl sulfates ("AS") in a ratio between about 1:1 and 1:0. The ratio of AES to AS is at least about 1:1, and the anionic surfactants can also be 100% AES and no AS (ratio of 1:0). The preferred AES:AS ratio is between about 1:1 and about 10:1, more preferably between about 2:1 and about 10:1, and most preferably between about 2:1 and about 6:1.

Alkyl ethoxylated sulfates and alkyl sulfates have the respective formulae (I) $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$ and (II) ROSO_3M , wherein R is alkyl or alkenyl of from about 9 to about 18 carbon atoms, x is 1 to 12, and M is H or a soluble salt-forming cation such as ammonium, alkanolamine such as triethanolamine, monovalent metals such as sodium and potassium, or polyvalent metal cations such as magnesium and calcium. The cation M of the anionic surfactant should be chosen such that the anionic surfactant is water soluble. Solubility will depend upon the particular mixture of anionic surfactants and cations chosen. As an aid to determining appropriate mixtures of anionic surfactants and cations, the anionic surfactants should be chosen such that the Krafft temperature of the surfactants is about 15°C or less, preferably about 10°C or less, more preferably about 0°C or less. It is also preferred that the anionic surfactants be soluble in the present shampoo compositions. Preferred cations for use in this invention are ammonium, sodium and/or magnesium.

The alkyl ethoxylated sulfates are typically made as condensation products of ethylene oxide and monohydric alcohols having from about 9 to about 18 carbon atoms. The alcohols can be derived from fats, e.g., coconut oil, palm kernel oil, or tallow, or can be synthetic. Such alcohols are preferably reacted with about 1 to about 10, more preferably from about 1 to about 4, most preferably from about 2 to about 3.5, molar proportions of ethylene oxide and the resulting mixture of molecular

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species having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

Suitable alkyl ethoxylated sulfates include, among others, sodium and ammonium salts of coconut alkyl triethylene glycol ether sulfate, tallow alkyl triethylene glycol ether sulfate, tallow alkyl hexaoxyethylene sulfate, and lauryl triethylene glycol ether sulfate. Preferred alkyl ethoxylated sulfates are sodium and ammonium salts of lauryl triethylene glycol ether sulfate, also known as "sodium" and "ammonium laureth-3 sulfate" or "sodium" and "ammonium lauryl (EO)₃ sulfate".

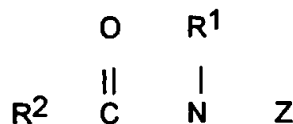
The alkyl sulfates are typically made by sulfating and neutralizing long chain alcohols. The alcohols can be derived from natural sources or can be synthetic alcohols. A variety of suitable commercial processes for manufacturing alkyl sulfates are well known to persons skilled in the field of surfactants.

Suitable alkyl sulfates include, among others, sodium and ammonium salts of lauryl sulfate, coconut alkyl sulfate, and tallow alkyl sulfate. Preferred for use in the present invention are sodium and ammonium salts of lauryl sulfate.

Polyhydroxy Fatty Acid Amide Surfactant

The surfactant system of the present shampoo compositions also comprises from about 1% to 20%, by weight of the surfactant system, preferably from about 5% to about 15% by weight, polyhydroxy fatty acid amide surfactants. It has been found that the amounts specified herein for the anionic surfactants and polyhydroxy fatty acid amide surfactants will provide shampoos that are mild, but that still provide high lathering and high deposition of functional materials.

The polyhydroxy fatty acid amide surfactant comprises compounds of the structural formula:



wherein: R¹ is H, C₁ - C₄ hydrocarbonyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferably C₁ - C₄ alkyl, more preferably C₁ alkyl (i.e., methyl); and R² is a C₅ - C₃₁ hydrocarbonyl moiety, preferably straight chain C₇ - C₁₉ alkyl or alkenyl, more preferably straight chain C₉ - C₁₇ alkyl or alkenyl, most preferably straight chain C₁₁ - C₁₆ alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbonyl moiety having a

linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of $-\text{CH}_2-(\text{CHOH})_n-\text{CH}_2\text{OH}$, $-\text{CH}(\text{CH}_2\text{OH})-(\text{CHOH})_{n-1}-\text{CH}_2\text{OH}$, and $-\text{CH}_2-(\text{CHOH})_2(\text{CHOR}')(\text{CHOH})-\text{CH}_2\text{OH}$, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide, and alkoxyated derivatives thereof. Most preferred are glycityls wherein n is 4, particularly $-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2\text{OH}$. R¹ can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl. R²-CO-N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide or tallowamide. Z can be, for example, 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl or 1-deoxymaltotriosityl.

Methods for making polyhydroxy fatty acid amides are known in the art. In general, they can be made by reacting an alkyl amine with a reducing sugar in a reductive amination reaction to form a corresponding N-alkyl polyhydroxyamine, and then reacting the N-alkyl polyhydroxyamine with a fatty aliphatic ester or triglyceride in a condensation/amidation step to form the N-alkyl, N-polyhydroxy fatty acid product. Processes for making compositions containing polyhydroxy fatty acid amides are disclosed, for example, in G.B. Patent Specification 809,060, published February 18, 1959, by Thomas Hedley & Co., Ltd., U.S. Patent 2,965,576, issued December 20, 1960 to E. R. Wilson, and U.S. Patent 2,703,798, Anthony M. Schwartz, issued December 25, 1934 to Piggott, each of which is incorporated herein by reference.

In one process for producing N-alkyl or N-hydroxyalkyl, N-deoxyglycityl fatty acid amides wherein the glycityl component is derived from glucose and the N-alkyl or N-hydroxyalkyl functionality is N-methyl,

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N- thyl, N-propyl, N-butyl, N-hydroxy thyl, or N-hydroxypropyl, the product is made by reacting N-alkyl- or N-hydroxyalkyl-glucamine with a fatty ester selected from fatty methyl esters, fatty ethyl esters, and fatty triglycerides in the presence of a catalyst selected from the group consisting of trilithium phosphate, trisodium phosphate, tripotassium phosphate, tetrasodium pyrophosphate, pentapotassium tripolyphosphate, lithium hydroxide, sodium hydroxide, potassium hydroxide, calcium hydroxide, lithium carbonate, sodium carbonate, potassium carbonate, disodium tartrate, dipotassium tartrate, sodium potassium tartrate, trisodium citrate, tripotassium citrate, sodium basic silicates, potassium basic silicates, sodium basic aluminosilicates, and potassium basic aluminosilicates, and mixtures thereof. The amount of catalyst is preferably from about 0.5 mole % to about 50 mole %, more preferably from about 2.0 mole % to about 10 mole %, on an N-alkyl or N-hydroxyalkyl-glucamine molar basis. The reaction is preferably carried out at from about 138°C to about 170°C for typically from about 20 to about 90 minutes. When triglycerides are utilized in the reaction mixture as the fatty ester source, the reaction is also preferably carried out using from about 1 to about 10 weight % of a phase transfer agent, calculated on a weight percent basis of total reaction mixture, selected from saturated fatty alcohol polyethoxylates, alkyloxyglucosides, linear glucamide surfactant, and mixtures thereof.

Preferably, this process is carried out as follows:

- (a) preheating the fatty ester to about 138°C to about 170°C;
- (b) adding the N-alkyl or N-hydroxyalkyl glucamine to the heated fatty acid ester and mixing to the extent needed to form a two-phase liquid/liquid mixture;
- (c) mixing the catalyst into the reaction mixture; and
- (d) stirring for the specified reaction time.

Also preferably, from about 2% to about 20% of preformed linear N-alkyl or N-hydroxyalkyl, N-linear glucosyl fatty acid amide product is added to the reaction mixture, by weight of the reactants, as the phase transfer agent if the fatty ester is a triglyceride. This seeds the reaction, thereby increasing reaction rate.

The polyhydroxy "fatty acid" amide materials used herein also offer the advantages to the shampoo formulator that they can be prepared

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wholly or primarily from natural, renewable, nonpetrochemical feedstocks and are degradable. They also exhibit low toxicity to aquatic life.

It should be recognized that along with the polyhydroxy fatty acid amides, the processes used to produce them will also typically produce quantities of nonvolatile by-product such as esteramides and cyclic polyhydroxy fatty acid amide. The level of these by-products will vary depending upon the particular reactants and process conditions. Preferably, the polyhydroxy fatty acid amide incorporated into the shampoo compositions herein will be provided in a form such that the polyhydroxy fatty acid amide contains less than about 10%, preferably less than about 4%, of cyclic polyhydroxy fatty acid amide. The preferred processes described above are advantageous in that they can yield rather low levels of by-products, including such cyclic amide by-product.

Optional Surfactants

Besides the above-mentioned surfactants which make up the "surfactant system" of the present shampoo compositions, the shampoos can also contain up to about 20% optional surfactants known to persons skilled in the art for use in shampoos, for example other anionics, nonionics, cationics, zwitterionics and/or amphoterics. Preferably the shampoos contain not more than about 15%, and most preferably not more than about 10% optional surfactants. A detailed description of various surfactants suitable for use in shampoos is disclosed in U.S. Patent 5,120,532 to Wells et al., issued June 9, 1992, at column 6, line 35 to column 14, line 17 (incorporated by reference herein). (As disclosed in the Wells et al. patent, certain cationic surfactants also act as conditioning agents; in such case, they are included in the present invention in the range of "conditioning agents" discussed below instead of "optional surfactants".)

Conditioning Agents

As discussed above, the present shampoo compositions contain from about 0.05% to about 25% by weight functional materials, preferably from about 0.1% to about 10% by weight.

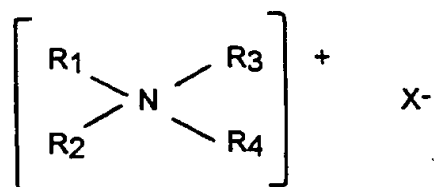
The functional materials can include one or more conditioning agents known to persons skilled in the art. Such conditioning agents are preferably used at levels between about 0.05% and about 8% by weight of the shampoo compositions, more preferably between about 0.2% and about 5% by weight, and most preferably between about 0.2% and about

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4% by weight. Preferred conditioning agents include cationic materials (cationic surfactants and cationic polymers), hydrocarbon oils, and blends of silicone oil and silicone gum.

Preferred cationic surfactants for use as conditioning agents in the present invention are quaternary ammonium or amino compounds having at least one N-radical containing one or more nonionic hydrophilic moieties selected from alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, and alkylester moieties, and combinations thereof. The surfactant contains at least one hydrophilic moiety within 4 (inclusive), preferably within 3 (inclusive), carbon atoms of the quaternary nitrogen or cationic amino nitrogen. For purposes herein, this means that the closest non-carbon atom in the hydrophilic moiety to the cationic nitrogen must be within the stated number of carbon atoms relative to said nitrogen. Additionally, carbon atoms that are part of a hydrophilic moiety, e.g., carbon atoms in a hydrophilic polyoxyalkylene (e.g., -CH₂-CH₂-O-), that are adjacent to other hydrophilic moieties are not counted as when determining the number of hydrophilic moieties within 4, or preferably 3, carbon atoms of the cationic nitrogen. In general, the alkyl portion of any hydrophilic moiety is preferably a C₁-C₃ alkyl. Suitable hydrophile-containing radicals include, for example, ethoxy, propoxy, polyoxyethylene, polyoxypropylene, ethylamido, propylamido, hydroxymethyl, hydroxyethyl, hydroxypropyl, methylester, ethylester, propylester, or mixtures thereof, as nonionic hydrophile moieties.

Among the quaternary ammonium cationic surfactants useful herein are those of the general formula:

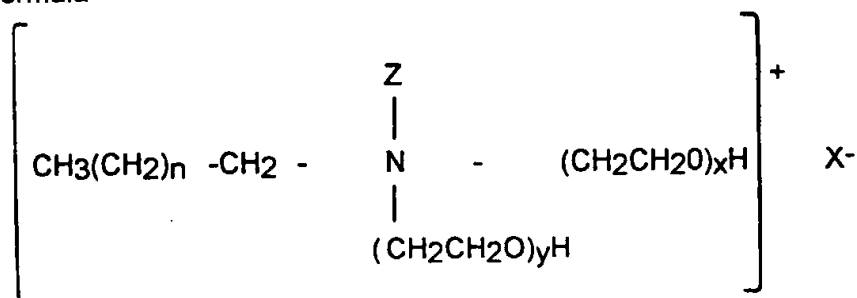


wherein R₁, R₂, R₃ and R₄ radicals comprise, independently, substituted or unsubstituted hydrocarbyl chains of from 1 to about 30 carbon atoms, or a hydrocarbyl having from 1 to about 30 carbon atoms and containing one or more aromatic, ether, ester, amido, or amino moieties present as substituents or as linkages in the radical chain, wherein at least one of the R₁-R₄ radicals contains one or more hydrophilic moieties selected from alkoxy (preferably C₁-C₃ alkoxy), polyoxyalkylene (preferably C₁-C₃

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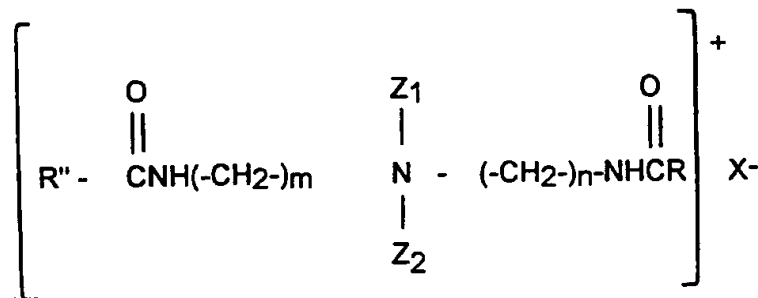
polyoxyalkyl ne), alkylamido, hydroxyalkyl, alkyl ster, and combinations thereof. Preferably, the cationic conditioning surfactant contains from 2 to about 10 nonionic hydrophile moieties located within the above stated ranges. For purposes herein, each hydrophilic amido, alkoxy, hydroxyalkyl, alkylester, alkylamido or other unit is considered to be a distinct nonionic hydrophile moiety. X is a soluble salt forming anion preferably selected from halogen (especially chlorine), acetate, phosphate, nitrate, sulfonate, and alkyl sulfate radicals.

Preferred quaternary ammonium salt surfactants include those of the formula



wherein n is from 8-28, preferably 16, x+y = 2 to about 15. Z is a short chain alkyl, preferably a C₁-C₃ alkyl, more preferably methyl, and X is a water soluble salt forming anion (e.g., Cl, sulfate, etc.)

Other preferred quaternary ammonium salt surfactants include those of the formula



wherein Z₁ and Z₂ are, independently, substituted or unsubstituted hydrocarbyls, and, preferably, Z₁ is an alkyl, preferably a C₁-C₃ alkyl, more preferably methyl, and Z₂ is a short chain hydroxyalkyl, preferably hydroxymethyl or hydroxyethyl, n and m independently are integers from 2 to 4, inclusive, preferably from 2 to 3, inclusive, more preferably 2, R' and R'', independently, are substituted or unsubstituted hydrocarbyls,

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preferably C₁₂-C₂₀ alkyl or alkenyl, and X is a soluble salt-forming anion (e.g., sulfate, Cl, etc.).

Specific examples of preferred quaternary ammonium salts include polyoxyethylene (2) stearyl methyl ammonium chloride, methyl bis (hydrogenated tallowamidoethyl) 2-hydroxyethyl ammonium methyl sulfate, polyoxypropylene (9) diethyl methyl ammonium chloride, tripolyoxyethylene (total PEG=10) stearyl ammonium phosphate, bis(N-hydroxyethyl -2-oleyl imidazolinium chloride) polyethylene glycol (12), and isododecylbenzyl triethanolammonium chloride. Particularly preferred is tricetyl methyl ammonium chloride ("TCMAC"), available commercially from Akzo-Chemie as ARQUAD-316 as a 90% suspension.

Another particularly preferred cationic surfactant is VARISOFT 110 (dihydrogenated tallowamidoethyl hydroxyethylmonium methosulfate).

The cationic polymer hair conditioning agents are water soluble, cationic organic polymers. The cationic polymers hereof will generally have a weight average molecular weight which is at least about 5,000, typically at least about 10,000, and is less than about 10 million. The cationic polymers will have cationic nitrogen-containing moieties such as quaternary ammonium or cationic amino moieties, or a mixture thereof. The cationic nitrogen-containing moiety will be present generally as a substituent, on a fraction of the total monomer units of the cationic hair conditioning polymers. Thus, the cationic polymer can comprise copolymers, terpolymers, etc. of quaternary ammonium or cationic amine-substituted monomer units and other non-cationic units referred to herein as spacer monomer units. Such polymers are known in the art, and a variety can be found in the *CTFA Cosmetic Ingredient Dictionary*, 3rd edition, edited by Estrin, Crosley, and Haynes (The Cosmetic, Toiletry, and Fragrance Association, Inc., Washington, D.C., 1982).

Suitable cationic hair conditioning polymers include, for example: copolymers of 1-vinyl-2-pyrrolidone and 1-vinyl-3-methyl-imidazolium salt (e.g., chloride salt) (referred to in the industry by the Cosmetic, Toiletry, and Fragrance Association, "CTFA", as Polyquaternium-16), such as those commercially available from BASF Wyandotte Corp. (Parsippany, NJ, USA) under the LUVIQUAT tradename (e.g., LUVIQUAT FC 370); copolymers of 1-vinyl-2-pyrrolidone and dimethylaminoethyl methacrylate (referred to in the industry by CTFA as Polyquaternium-11) such as those commercially available from Gaf Corporation (Wayne, NJ, USA) under the

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GAFQUAT tradenam (e.g., GAFQUAT 755N); polymeric quaternary ammonium compounds such as guar hydroxypropyltrimonium chloride (commercially available from Rhone-Poulenc in their JAGUAR series); cationic diallyl quaternary ammonium-containing polymers, including, for example, dimethyldiallylammonium chloride homopolymer and copolymers of acrylamide and dimethyldiallylammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively; and mineral acid salts of amino-alkyl esters of homo- and co-polymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, as described in U.S. Patent 4,009,256, incorporated herein by reference.

Other cationic polymers that can be used include polysaccharide polymers, such as cationic cellulose derivatives and cationic starch derivatives. Cationic cellulose as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10, is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR and LR series of polymers, and from Union Carbide Corp. (Danbury, Connecticut, USA) under their UCARE POLYMER JR series of materials, e.g., UCARE POLYMER JR-30M, JR-125 and JR-400. Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. (Edison, NJ, USA) under the tradename Polymer LM-200.

Organic hair conditioning agents can also be used as conditioning agents in the present shampoo compositions. The organic hair conditioning materials hereof include liquids selected from the group consisting of hydrocarbon oils and fatty esters. Hydrocarbon oils include cyclic hydrocarbons, straight chain aliphatic hydrocarbons (saturated or unsaturated), and branched chain aliphatic hydrocarbons (saturated or unsaturated). Straight chain hydrocarbon oils will preferably contain from about 12 to about 19 carbon atoms, while branched chain hydrocarbon oils can and typically may contain higher numbers of carbon atoms. Also encompassed herein are polymeric hydrocarbons of alkenyl monomers, such as C₂-C₆ alkenyl monomers. These polymers can be straight or branched chain polymers. The straight chain polymers will typically be

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relatively short in length, having a total number of carbon atoms as described above for straight chain hydrocarbons in general. The branched chain polymers can have substantially higher chain length. The number average molecular weight of such materials can vary widely, but will typically be up to about 500, preferably from about 200 to about 400, more preferably from about 300 to about 350. Specific examples of suitable materials include mineral oil (preferred), paraffin oil, saturated and unsaturated dodecane, saturated and unsaturated tridecane, saturated and unsaturated tetradecane, saturated and unsaturated pentadecane, saturated and unsaturated hexadecane, and mixtures thereof. Branched-chain isomers of these compounds, as well as of higher chain length hydrocarbons, can also be used. Exemplary branched-chain isomers are highly branched saturated or unsaturated alkanes, such as the permethyl-substituted isomers, e.g., the permethyl-substituted isomers of hexadecane and eicosane, such as 2, 2, 4, 4, 6, 6, 8, 8-dimethyl-10-methylundecane and 2, 2, 4, 4, 6, 6-dimethyl-8-methylnonane, sold by Permethyl Corporation. Polymeric hydrocarbon oils are also useful conditioning agents. A preferred hydrocarbon polymer is polybutene, such as the copolymer of isobutylene and butene; a commercially available material of this type is Indopol L-14 polybutene from Amoco Chemical Co. (Chicago, Illinois, U.S.A.). Other polymeric conditioners can include polyisoprene, polybutadiene, and other hydrocarbon polymers of C₄ to C₁₂ straight and branched chain, mono- and di-unsaturated aliphatic monomers, and derivatives thereof.

The fatty esters useful as conditioning agents are characterized by having at least 10 carbon atoms, and include esters with hydrocarbyl chains derived from fatty acids or alcohols, e.g., mono-esters, polyhydric alcohol esters, and di- and tri-carboxylic acid esters. The hydrocarbyl radicals of the fatty esters hereof can also include or have covalently bonded thereto other compatible functionalities, such as amides and alkoxy moieties (e.g., ethoxy or ether linkages, etc.).

Other suitable conditioning agents for use in the present shampoo compositions include water insoluble, nonvolatile silicone hair conditioning agents. The silicone conditioning agent will comprise a silicone fluid and can also comprise other ingredients, such as a silicone resin to enhance silicone fluid deposition efficiency and enhance glossiness of the hair (especially when high refractive index, e.g. above

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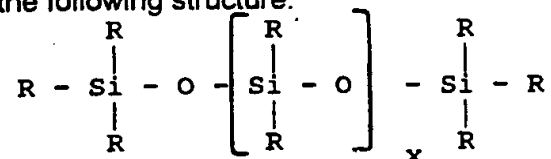
about 1.46, silicon conditioning agents are used, e.g. highly phenylated silicones).

The silicone hair conditioning agent may also comprise volatile silicone components. Typically, if volatile silicones are present, it will be incidental to their use as a solvent or carrier for commercially available forms of nonvolatile silicone materials ingredients, such as silicone gums and resins.

The silicone hair conditioning agent component will generally be used in the shampoo compositions hereof at levels of from about .05% to about 10% by weight of the composition, preferably from about 0.1% to about 8%, more preferably from about 0.1% to about 5%, most preferably from about 0.1% to about 4%.

One type of silicone fluid that can be used herein is a silicone oil. The term "silicone oil" shall mean flowable silicone materials having a viscosity of less than 1,000,000 centistokes at 25°C. Generally, the viscosity of the fluid will be between about 5 and 1,000,000 centistokes at 25°C, preferably between about 10 and about 100,000. Suitable silicone oils include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and mixtures thereof. Other insoluble, nonvolatile silicone fluids having hair conditioning properties can also be used.

More particularly silicone oils hereof include polyalkyl or polyaryl siloxanes with the following structure:



wherein R is aliphatic, preferably alkyl or alkenyl, or aryl, R can be substituted or unsubstituted, and x is an integer from 1 to about 8,000. Suitable unsubstituted R groups include alkoxy, aryloxy, alkaryl, arylalkyl, arylalkenyl, alkamino, and ether-substituted, hydroxyl-substituted, and halogen-substituted aliphatic and aryl groups. Suitable R groups also include cationic amines and quaternary ammonium groups.

The aliphatic or aryl groups substituted on the siloxane chain may have any structure as long as the resulting silicones remain fluid at room temperature, are hydrophobic, are neither irritating, toxic nor otherwise harmful when applied to the hair, are compatible with the other components of the composition, are chemically stable under normal use

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and storage conditions, are insoluble in the composition, and are capable of being deposited on and, of conditioning, the hair.

The two R groups on the silicon atom of each monomeric silicone unit may represent the same group or different groups. Preferably, the two R groups represent the same group.

Preferred alkyl and alkenyl substituents are C₁-C₅ alkyls and alkenyls, more preferably from C₁-C₄, most preferably from C₁-C₂. The aliphatic portions of other alkyl-, alkenyl-, or alkynyl-containing groups (such as alkoxy, alkaryl, and alkamino) can be straight or branched chains and preferably have from one to five carbon atoms, more preferably from one to four carbon atoms, even more preferably from one to three carbon atoms, most preferably from one to two carbon atoms. As discussed above, the R substituents hereof can also contain amino functionalities, e.g. alkamino groups, which can be primary, secondary or tertiary amines or quaternary ammonium. These include mono-, di- and tri- alkylamino and alkoxyamino groups wherein the aliphatic portion chain length is preferably as described above. The R substituents can also be substituted with other groups, such as halogens (e.g. chloride, fluoride, and bromide), halogenated aliphatic or aryl groups, and hydroxy (e.g. hydroxy substituted aliphatic groups). Suitable halogenated R groups could include, for example, tri-halogenated (preferably fluoro) alkyl groups such as -R¹-C(F)₃, wherein R¹ is C₁-C₃ alkyl. Examples of such polysiloxanes include polymethyl -3,3,3 trifluoropropylsiloxane.

The nonvolatile polyalkylsiloxane oils that may be used include, for example, polydimethylsiloxanes. These siloxanes are available, for example, from the General Electric Company in their Viscasil R and SF 96 series, and from Dow Corning in their Dow Corning 200 series. Polydimethylsiloxane oil is also known as "dimethicone" oil.

The polyalkylaryl siloxane oils that may be used, also include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

The polyether siloxane copolymers that may be used include, for example, a polypropylene oxide modified polydimethylsiloxane (e.g., Dow Corning DC-1248) although ethylene oxide or mixtures of ethylene oxide and propylene oxide may also be used.

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Another silicone fluid that can be specially useful in the silicon conditioning agents is insoluble silicone gum. The term "silicone gum", as used herein, means polyorganosiloxane materials having a viscosity at 25 °C of greater than or equal to 1,000,000 centistokes. Silicone gums are described by Petrarch and others including U.S. Patent 4,152,416, Spitzer et al., issued May 1, 1979 and Noll, Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968. Also describing silicone gums are General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. All of these described references are incorporated herein by reference. The "silicone gums" will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and about 1,000,000. Specific examples include polydimethylsiloxane, (polydimethylsiloxane) (methylvinylsiloxane) copolymer, poly(dimethylsiloxane) (diphenyl siloxane)(methylvinylsiloxane) copolymer and mixtures thereof. Polydimethylsiloxane gum is also known as "dimethicone" gum.

Preferably the silicone hair conditioning agent comprises a mixture of a polydimethylsiloxane gum, having a viscosity greater than about 1,000,000 centistokes and polydimethylsiloxane oil having a viscosity of from about 10 centistokes to about 100,000 centistokes, wherein the ratio of gum to fluid is from about 30:70 to about 70:30, preferably from about 40:60 to about 60:40.

Silicone hair conditioning agents are described in more detail in U.S. Patent 5,100,657 to Ansher-Jackson et al., issued March 31, 1992, at column 13, line 65 to column 18, line 47 (incorporated by reference herein).

Further descriptions of many different kinds of conditioning agents suitable for use in the present invention are found in the following patents (incorporated by reference herein): U.S. Patent 5,100,657 to Ansher-Jackson et al., issued March 31, 1992; U.S. Patent 5,106,609 to Bolich, Jr. et al., issued April 21, 1992; and U.S. Patent 5,120,532 to Wells et al., issued June 9, 1992.

A preferred shampoo composition according to the present invention includes a mixture of the following functional materials to be deposited on the hair: guar hydroxypropyltrimonium chloride (preferably at a level between about 0.05% and about 0.70% by weight), hydrocarbon oil (preferably at a level between about 0.10% and about 1.40% by

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w ight), and a blend of dimethicone oil and dimethicone gum (preferably at a level between about 0.1% and about 4.0% by weight).

Antidandruff Agents

Antidandruff agents can also be used as functional materials in the present shampoo compositions. Suitable antidandruff agents include, for example, sulfur, selenium sulfide, and pyridinethione salts. Preferred are heavy metal salts of 1-hydroxy-2-pyridinethione and selenium disulfide. The antidandruff agents are preferably used at levels of about 0.1% to about 5%, more preferably from about 0.3% to about 5%, by weight of the shampoo compositions.

Selenium sulfide is a staple item of commerce. It is generally regarded as a compound having one mole of selenium and two moles of sulfur. However, it may take the form of a cyclic structure, Se_xS_y , wherein $x + y = 8$. U.S. Patent 2,694,668, Baldwin et al., issued November 16, 1954; U.S. Patent 3,152,046, Kapral, issued October 6, 1984; U.S. Patent 4,089,945, Brinkman, issued May 16, 1978; and U.S. Patent 4,885,107, Wetzell, issued December 12, 1989, all incorporated herein by reference, disclose selenium disulfide as an active ingredient in antidandruff shampoo compositions. Selenium sulfide (selenium disulfide) preferably has an average of less than about 15μ , more preferably less than about 10μ . These measurements can be made using a forward laser light scattering device (e.g., a Malvern 3600 instrument).

Preferred pyridinethione antidandruff agents are water insoluble 1-hydroxy-2-pyridinethione salts. Preferred salts are formed from heavy metals such as zinc, tin, cadmium, magnesium, aluminum and zirconium. The most preferred metal herein is zinc. The most preferred active is the zinc salt of 1-hydroxy-2-pyridinethione, often referred to as zinc pyridinethione (ZPT). Other cations such as sodium may also be suitable. These types of antidandruff agents are well known in the art. 1-hydroxy-2-pyridinethione salts are disclosed for use in antidandruff shampoos in U.S. Patent 2,809,971, Bernstein, issued October 15, 1957; U.S. Patent 3,236,733, Karsten et al., issued February 22, 1966; U.S. Patent 3,753,196 Parran, issued August 21, 1973; U.S. Patent 3,761,418, Parran, issued September 25, 1973; U.S. Patent 4,345,080, Bolich, issued August 17, 1982; U.S. Patent 4,323,683, Bolich et al., issued April 6, 1982; U.S. Patent 4,379,753, Bolich, issued April 12, 1983; and U.S. Patent 4,470,982, Winkel, issued September 11, 1984; all incorporated

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herein by reference. Particularly preferred are those 1-hydroxy-2-pyridinethione salts in platelet particle form, wherein the particles have an average size of up to about 20 microns, preferably up to about 8 microns, most preferably up to about 5 microns.

Hair Styling Agents

The functional materials used in the present shampoo compositions can also include one or more hair styling agents, which are a class of materials which are designed to assist the user in having the shampooed hair retain a particular shape. Preferably hair styling agents are used at levels between about 0.2% and about 20% by weight of the shampoo compositions, more preferably between about 2% and about 6%.

The hair styling agents can be selected from various resins and gums. Preferred styling agents used herein comprise shampoo-compatible polymers which, in general, are homopolymers or copolymers of hydrophobic monomers. Alternatively, hydrophilic polymers useful as styling agents herein can be a copolymer of a hydrophilic monomer and a hydrophobic monomer, or mixtures thereof. Examples of complex polymer systems are found in U.S. Patent 3,222,329 to Grosser et al., issued December 7, 1965; U.S. Patent 3,577,517 to Kubot et al., issued May 4, 1971; U.S. Patent 4,012,501 to Farber, issued March 15, 1977; U.S. Patent 4,272,511 to Papantoniou and Mondet, issued June 9, 1981; and U.S. Patent 4,196,190, to Gehman et al., issued April 1, 1980. Examples of block polymer systems are found in U.S. Patent 3,907, 984 to Calvert et al., issued September 23, 1975; U.S. Patent 4,030,512 to Papantoniou et al., issued June 21, 1977; and U.S. Patent 4,283,384 to Jacquet et al., issued August 11, 1981.

Preferred hair styling polymers for use as styling agents in the present invention are disclosed in U.S. Patent 5,120,531 to Wells et al., issued June 9, 1992, at column 2, line 35 to column 4, line 68; and polymer solvents are disclosed at column 5, line 1 to column 6, line 16 (all incorporated by reference herein).

Water

The shampoo compositions of the present invention will comprise from about 35% to about 95%, by weight, water. Preferably the shampoo compositions comprise from about 50% to about 85% water, and most preferably from about 60% to about 80%.

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The pH of the shampoo compositions is not critical and can be in the range of from about 2 to about 10, preferably from about 4 to about 8, and more preferably from about 5.5 to about 8.

Optional Ingredients

A variety of other optional ingredients can also be used in the present shampoo compositions. Such optional ingredients include, for example, preservatives such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; quaternary polymeric foam boosters, preferably from about 0.01% to about 0.2% by weight of the composition; fatty alcohols; block polymers of ethylene oxide and propylene oxide such as Pluronic F88 offered by BASF Wyandotte; ammonium xylene sulfonate; propylene glycol; polyvinyl alcohol; ethyl alcohol; pH adjusting agents such as monosodium phosphate, disodium phosphate, citric acid, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate, etc.; sequestering agents such as ethylenediamine tetraacetate ("EDTA"); thickening agents such as sodium chloride; perfumes; and dyes. These optional ingredients are typically used at levels of from about 0.01% to about 10% of the composition. This list of optional ingredients is not meant to be exclusive, and other optional components can be utilized.

The present shampoo compositions optionally include a suspending agent useful for suspending particulate antidandruff agents (or other functional materials) and for thickening the compositions, at a level typically between about 0.5% and about 10% by weight of the shampoo. Preferred crystalline suspending agents are long chain acyl derivative materials and long chain amine oxides, as well as mixtures of such materials. Included are ethylene glycol long chain esters, alkanol amides of long chain fatty acids, long chain esters of long chain fatty acids, glyceryl long chain esters, long chain esters of long chain alkanolamides, and long chain alkyl dimethyl amine oxides, and mixtures thereof. Examples of crystalline suspending agents are described in U.S. Patent 4,741,855, Grote and Russell, issued May 3, 1988, incorporated herein by reference. Other optional suspending agents that can be used include polymeric thickeners, such as carboxyvinyl polymers. Preferred carboxyvinyl polymers are copolymers of acrylic acid crosslinked with polyallylsucrose as described in U.S. Patent 2,798,053, Brown, issued July 2, 1957, incorporated herein by reference. These

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polymers are provided by B. F. Goodrich Company as, for example, Carbopol 934, 940, 941, and 956.

Other materials can also be used as optional suspending agents include those that can impart a gel-like viscosity to the composition, such as water soluble or colloiddally water soluble polymers like cellulose ethers (e.g., hydroxyethyl cellulose), guar gum, polyvinyl alcohol, polyvinyl pyrrolidone, hydroxypropyl guar gum, starch and starch derivatives, and other thickeners, viscosity modifiers, gelling agents, etc. Mixtures of these materials can also be used. Another type of suspending agent that can be used is xanthan gum. Shampoo compositions utilizing xanthan gum as a suspending agent for the silicone hair conditioning component are described in U.S. Patent 4,788,006, Bolich and Williams, issued November 29, 1988, incorporated herein by reference. Kelco, a Division of Merck & Co., Inc. offers xanthan gum as KeltrolR. The xanthan gum, when used as the silicone hair conditioning component suspending agent, will typically be present in pourable, liquid formulations at a level of from about 0.02% to about 3%, preferably from about 0.03% to about 1.2%, in the compositions of the present invention.

The following Examples further describe and demonstrate the preferred embodiments within the scope of the present invention. The Examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention as many variations thereof are possible without departing from its spirit and scope.

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EXAMPLES 1-4

Shampoo compositions of the present invention are prepared as follows. The percentages given are percentages by weight of the shampoo compositions.

<u>Component</u>	<u>Example Number</u>			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Ammonium Lauryl Sulfate	6.6	2.5	2.3	3.5
Ammonium Lauryl (EO) ₃ Sulfate	12.1	15.0	12.8	8.4
Lauryl N-Methyl Glucamide	2.0	2.5	2.0	2.1
Dimethicone Blend ¹	0.8	0.5	0.5	1.0
Guar Gum Derivative ²	—	0.2	—	—
Hydrocarbon Oil ³	—	0.4	—	—
Fatty Alcohols	—	—	0.6	0.6
Ethylene Glycol Distearate	1.5	1.5	2.0	1.5
Disodium EDTA	0.1	0.1	0.1	0.1
Monosodium Phosphate and				
Disodium Phosphate	0.4	0.4	0.4	0.4
Sodium Chloride	1.0	1.0	1.0	1.0
Color Solution	0.1	0.1	0.1	0.1
Perfume Solution	0.7	0.7	0.7	1.0
Water and Minors	<u>74.7</u>	<u>75.1</u>	<u>77.5</u>	<u>80.3</u>
Total	100.0	100.0	100.0	100.0

¹ A 40(gum)/60(oil) weight ratio blend of SE-76 dimethicone gum available from General Electric Silicones Division and a dimethicone oil having a viscosity of 350 centistokes.

² Jaguar C-17, tradename for guar hydroxypropyltrimonium chloride, a cationic polymer available from Rhone-Poulenc (Cranbury, NJ, USA).

³ Indopol L-14 polybutene available from Amoco Chemical Co. (Chicago, IL, USA).

The example compositions hereof can be made by preparing in a premix tank the following additions while mixing and heating to 72°C:

- a) Part of Ammonium Lauryl (EO)₃ Sulfate
- b) All of the Lauryl N-Methyl Glucamide
- c) Part of the Water.

When the content reaches 72°C, start adding:

- d) Guar Gum Derivative

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-) Hydrocarbon Oil
- f) Fatty Alcohols
- g) Disodium EDTA
- h) Monosodium Phosphate and Disodium Phosphate
- i) Ethylene Glycol Distearate

Mix for at least 30 minutes. After 30 minutes, cool down the mixture to approximately 30°C using a high shear mixer before passing through a heat exchanger. Then add the following materials:

- j) All of the Ammonium Lauryl Sulfate
- k) The Remaining Part of the Ammonium Lauryl (EO)₃ Sulfate
- l) Dimethicone Blend
- m) Sodium Chloride
- n) Color Solution
- o) Perfume Solution
- p) Water and Minors

The shampoo compositions are mild and provide high lathering properties. Additionally, the shampoo compositions provide high deposition of the functional materials (the dimethicone blend, guar gum derivative and hydrocarbon oil).

WHAT IS CLAIMED IS:

1. A shampoo composition comprising:
 - (a) from about 5% to about 40%, by weight, surfactant system comprising: (i) from 80% to about 99%, by weight of the surfactant system, anionic surfactants which are alkyl ethoxylated sulfates and alkyl sulfates in a ratio between about 1:1 and 1:0; and (ii) from about 1% to 20%, by weight of the surfactant system, polyhydroxy fatty acid amide surfactants;
 - (b) from about 0.05% to about 25%, by weight, functional materials; and
 - (c) from about 35% to about 95%, by weight, water.
2. A shampoo composition according to Claim 1 wherein the ratio of alkyl ethoxylated sulfates to alkyl sulfates is between about 1:1 and about 10:1.
3. A shampoo composition according to Claim 1 which comprises from about 7% to about 35% by weight surfactant system.
4. A shampoo composition according to Claim 1 which comprises from about 85% to about 95%, by weight of the surfactant system, anionic surfactants selected from the group consisting of alkyl ethoxylated sulfates, alkyl sulfates, and mixtures thereof.
5. A shampoo composition according to Claim 1 which comprises from about 5% to about 15%, by weight of the surfactant system, polyhydroxy fatty acid amide surfactants.
6. A shampoo composition according to Claim 1 wherein the polyhydroxy fatty acid amide surfactants are glucose amides.
7. A shampoo composition according to Claim 1 wherein the alkyl ethoxylated sulfates are selected from the group consisting of sodium lauryl triethylene glycol ether sulfate and ammonium lauryl triethylene glycol ether sulfate, and mixtures thereof.
- 5 8. A shampoo composition according to Claim 1 wherein the alkyl sulfates are selected from the group consisting of sodium lauryl sulfate and ammonium lauryl sulfate, and mixtures thereof.
9. A shampoo composition according to Claim 1 comprising from about 0.1% to about 10% by weight functional materials.

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10. A shampo composition according to Claim 1 wherein the functional materials include conditioning agents present at a level between about 0.05% and about 8% by weight of the shampoo compositions.
11. A shampoo composition according to Claim 10 wherein the conditioning agents are a mixture of guar hydroxypropyltrimonium chloride, hydrocarbon oil, and a blend of dimethicone oil and dimethicone gum.
12. A shampoo composition according to Claim 1 wherein the functional materials include hair styling agents present at a level between about 2% and about 6% by weight of the shampoo compositions.
13. A shampoo composition according to Claim 1 wherein the functional materials include antidandruff agents present at a level between about 0.1% and about 5% by weight of the shampoo compositions.
14. A shampoo composition according to Claim 1 comprising from about 50% to about 85% by weight water.

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INTERNATIONAL SEARCH REPORT

Internat Application No
PCT/US 94/14289

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,92 05764 (PROCTER & GAMBLE) 16 April 1992 see the whole document ---	1-14
A	WO,A,93 19149 (PROCTER & GAMBLE) 30 September 1993 see the whole document -----	1-14

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
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21 April 1995

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat Application No

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		JP-T-	6501699	24-02-94
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